

The limitations on organic detection in Mars-like soils by thermal volatilization–gas chromatography–MS and their implications for the Viking results

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The failure of Viking Lander thermal volatilization (TV) (without or with thermal degradation)–gas chromatography (GC)–MS experiments to detect organics suggests chemical rather than biological interpretations for the reactivity of the martian soil. Here, we report that TV–GC–MS may be blind to low levels of organics on Mars. A comparison between TV–GC–MS and total organics has been conducted for a variety of Mars analog soils. In the Antarctic Dry Valleys and the Atacama and Libyan Deserts we find 10–90 μg of refractory or graphitic carbon per gram of soil, which would have been undetectable by the Viking TV–GC–MS. In iron-containing soils (jarosites from Rio Tinto and Panoche Valley) and the Mars simulant (palagonite), oxidation of the organic material to carbon dioxide (CO_2) by iron oxides and/or their salts drastically attenuates the detection of organics. The release of 50–700 ppm of CO_2 by TV–GC–MS in the Viking analysis may indicate that an oxidation of organic material took place. Therefore, the martian surface could have several orders of magnitude more organics than the stated Viking detection limit. Because of the simplicity of sample handling, TV–GC–MS is still considered the standard method for organic detection on future Mars missions. We suggest that the design of future organic instruments for Mars should include other methods to be able to detect extinct and/or extant life.

astrobiology | detection of organics | search for martian life | extreme environments | deserts

In 1976, the Viking Landers carried out an extensive set of biological experiments to search for the presence of extant life on the surface of Mars (1). In addition, a series of molecular analysis experiments were conducted to search for the presence of organic compounds in the martian soil (2). The biological tests consisted of three independent experiments designed to detect Earth-like microorganisms in the top few centimeters of the martian soil. The gas exchange experiment was designed to determine whether martian life could metabolize and exchange gaseous products in the presence of water vapor and in a nutrient solution (3); the carbon assimilation experiment was based on the assumption that martian life would have the capability to incorporate radioactively labeled carbon dioxide and/or monoxide in the presence of sunlight (i.e., photosynthesis) (4); and the labeled release (LR) experiment sought to detect heterotrophic metabolism by the release of radioactively labeled carbon initially incorporated into organic compounds in a nutrient solution (5). At both Viking landing sites the three biological experiments yielded positive responses demonstrating the presence of a highly reactive soil. Surprisingly, the LR experiment was suggestive of the possible presence of biological activity in the martian soil. However, the most puzzling result came from the molecular analysis experiments (2, 6) performed in the

martian soil: three sample analyses from surface material from the Viking 1 and 2 sites and another from underneath a rock from the Viking 2 site. In these experiments, soil was subjected to thermal volatilization (TV)–gas chromatography (GC)–MS; this assay consisted of a rapid heating of the soil to vaporize small molecules and break down larger ones into smaller organic molecules, and the resultant fragments were separated by GC and analyzed by MS. Unexpectedly, in none of the experiments performed in both landing sites could organic material be observed at detection limits generally of the order of parts per billion for molecules larger than two carbon atoms and of parts per million for some smaller molecules. The evolution of CO_2 and H_2O , but not of other inorganic gases, was observed upon heating the soil sample at 200°C, 350°C, and 500°C. One important concern was whether the GC–MS instrument worked properly. Fortunately, experimental data existed that demonstrated the proper function of the instrument beyond any doubt (7). Traces of some organic solvents that were used during the cleaning of the instruments before they were incorporated into the Landers were detected in the background, such as methyl chloride (15 parts per billion) and perfluoroethers (1–50 parts per billion). These contaminants were previously detected in preflight and cruise tests. Therefore, the detection of these contaminants demonstrated that the instruments worked well. Consequently, the presence of life in the martian soil was in apparent contradiction with the results from the TV–GC–MS. The lack of organics in the TV–GC–MS experiment was used as the most compelling argument against the presence of extant life on the surface of Mars.

The reactivity of the martian soil observed in the three biological experiments (3–5) was subsequently explained by the presence of one or more inorganic oxidants (e.g., superoxides, peroxides, and peroxy nitrates) at the parts per million level. The lack of organics in the martian soil could also be explained by their oxidation to carbon dioxide due to the presence of such oxidants and/or direct UV radiation damage (8). There have been many suggestions regarding the nature of the chemical

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Abbreviations: LR, labeled release; TV, thermal volatilization; GC, gas chromatography; NASA, National Aeronautics and Space Administration.

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Table 1. Total organic matter (TOM) present in different Mars analogs soils and its detection by TV-GC-MS

Soil sample	TOM, μg of C per gram of soil	$\delta^{13}\text{C}$	C/N ratio	TV-GC-MS, * 500°C, μg of benzene per gram of soil	TV-GC-MS, * 750°C, μg of benzene per gram of soil
Antarctic Desert					
Dry Valley	20–30	–25.03	0.9	N.D.	N.D.
Dry Valley (sample no. 726)	60–90	–24.34	0.3	N.D.	N.D.
Otway massif mill stream glacier	10–20	–25.13	1.0	N.D.	N.D.
Atacama Desert					
Yungay, Chile (AT02-03A)	20–40	–26.09	8.2	N.D.	1–4
La Joya, Peru (PC03-06)	20–30	–21.04	0.3	N.D.	1–4
Las Juntas, Chile (AT02-22)	400–440	–28.93	16.7	1.0–3.0	70–200
Libyan Desert					
SA05-01	30–40	–23.43	>30	N.D.	N.D.
SA05-02	50–60	–21.62	>30	N.D.	N.D.
SA05-03	60–70	–20.06	>30	N.D.	N.D.
Mojave Desert (DV02-10)	145–260	–24.84	9.5	N.D.	15–100
Minas de Rio Tinto					
Sediment (RT04-01)	1050–1400	–24.34	11.4	5–50	50–100
Evaporite (RT04-02)	1200–1500	–23.34	8.2	7–80	70–100
Panoche Valley (PA04-01)	140–180	–27.37	7.4	N.D.	5–20
NASA Mars-1 martian soil simulant	1200–1400	–24.13	11.2	N.D.	100–150

N.D., not detected.

*Benzene was the major organic compound detected. One microgram of benzene is equivalent to 0.92 μg of C.

reactivity of the martian soil, but no laboratory experiment has yet been able to simulate both the gas exchange (3) and the LR response (5). Instruments built to further investigate the reactive nature of the martian soil [e.g., Mars Oxidant Experiment for the ill-fated Russian Mars 1996 mission (8) and Mars Oxidant Instrument for the European Space Agency ExoMars 2011 (9)] have not yet performed *in situ* experiments on Mars. Mars Oxidant Instrument has been successfully tested in the Mars-like soils of the Atacama Desert, where the oxidative nature of the soil is thought to be triggered by strong acids (e.g., sulfuric and nitric acids) depositing from the atmosphere (9).

A recent evaluation of the oxidative destruction mechanisms of meteoritic organics on the surface of Mars suggests that the end products are salts of aliphatic and aromatic polycarboxylic acids (10). Such compounds are refractory organics (e.g., non-volatile and thermally stable) under the temperatures reached by the molecular analysis experiments, and consequently they were missed by the Viking TV-GC-MS (10). Alternatively, the absence of organics in the soil at parts per billion levels does not preclude the presence of extant life in the martian surface. Klein (11) pointed out that the Viking TV-GC-MS would not detect *Escherichia coli* at levels of 10^6 per gram, which has been confirmed by recent simulations (12).

The search for organics on Mars continues to be a key science goal for future missions. Because of the simplicity of sample handling, TV-GC-MS has still been considered the standard method for organic detection on Mars; for instance, the ill-fated Beagle Lander carried a combustion-MS, the Thermal Evolved Gas Analyzer instrument on the 2007 Phoenix mission is a thermal analysis and MS, the basic unit on the Sample Analysis at Mars instrument selected for the upcoming 2009 Mars Science Laboratory mission is a TV-GC-MS, and the Mars Organic Detector unit for the 2011 European Space Agency ExoMars mission is a TV coupled to capillary electrophoresis with a fluorescence detector. We report here results of studies on several Mars analog soils in which we compare the detection of organics by TV-GC-MS with total organic analysis of the samples. We analyzed samples from the dry Mars-like environments of the Dry Valleys in Antarctica (13) and the Atacama Desert (14) in Chile and Peru, where environmental conditions

result in soils with low biological and organic content, and the Libyan Desert in Egypt, which is part of the hyperarid Sahara. For comparison, we also analyzed samples from wetter desert areas in the Atacama and Mojave (in the southwestern U.S.) Deserts. We also analyzed samples of jarosite-containing soils from the Rio Tinto in Spain (15) and the Panoche Valley in California (16). These soils may be analogs for the soils detected by the Mars exploration rover at the Meridiani Planum site on Mars (17). In addition, we analyzed samples of the National Aeronautics and Space Administration (NASA) Mars-1 martian soil simulant, which is derived from Hawaiian palagonite (18).

Results and Discussion

All samples were analyzed for total organic matter, $\delta^{13}\text{C}$, C/N ratio, and their response in TV-GC-MS at 500°C (Viking protocol) and 750°C. A summary of the results is listed in Table 1. The total organic matter varied from 10 to 1,500 μg of C per gram of soil depending on the environment. In all cases, the $\delta^{13}\text{C}$ values varied from –28.93 to –20.06, a typical range for organic matter produced by C_3 photosynthesis (19). Similarly, the C/N ratio for most samples is typical of soil organic matter, 9–30 (20), except in Antarctica and La Joya, where the ratio is ≤ 1 . Surprisingly, the production of benzene, a major organic compound resulting from TV-GC-MS was not correlated with the amount of organic matter present originally in the soil. The samples from the Dry Valleys of Antarctica (cold desert) and the arid core regions of the Atacama (temperate desert) and the Libyan (hot desert) contain very low levels of organics from 20 to 90 μg of C per gram of soil. Antarctic sample 726 is of particular interest because it was one of the prelaunch test samples for the Viking mission. Interestingly, this was the only terrestrial sample testing by Viking that did not contain organics detectable by the TV-GC-MS (21) yet did give a positive result for the LR experiment (22). Subsequent analysis has shown that this soil contains primarily metamorphosed coal, kerogen (John R. Cronin, personal communication), and some low levels of amino acids (23). We also found that TV-GC-MS of this sample, even at temperatures higher than used by Viking (up to 750°C), yielded no detectable organics. Other soils from the Antarctic

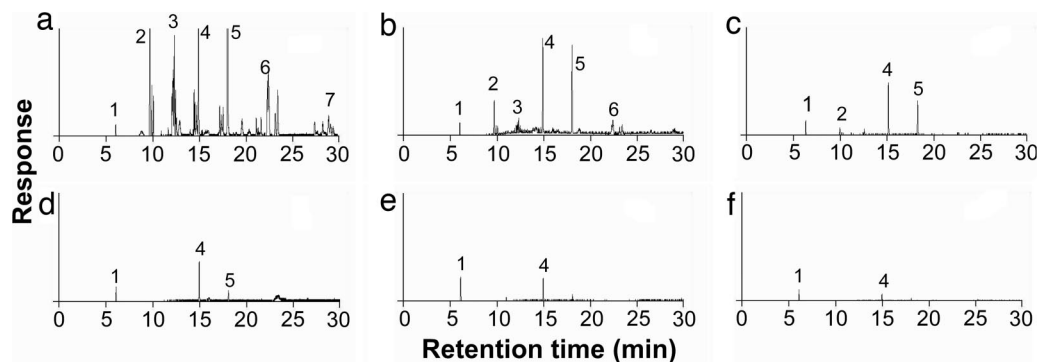


Fig. 4. Reconstructed ion gas chromatograms of the volatile fraction released during flash TV. The sample consisted of stearic acid doped in an organic-free NASA Mars-1 martian soil simulant at 750°C in an inert atmosphere composed of helium: 50 (a), 10 (b), 5 (c), 1 (d), 0.5 (e), and 0.1 (f) mg of C per gram of simulant. Peaks: 1, formic acid; 2, 1-butene; 3, 2-pentene; 4, benzene; 5, methylbenzene; 6, ethylbenzene; 7, methylethylbenzene. For simplicity, only the major peaks are labeled in the chromatograms. The NASA Mars-1 martian soil simulant was thoroughly washed with methylene chloride/methanol (2:1) over 24 h to remove the organics in a Soxhlet apparatus. The gas chromatograms of this martian soil simulant after solvent cleaning did not show organics by TV-GC-MS.

the bulk composition of the soils at the Viking landing sites (18). Because this soil is from Hawaii, it is not surprising that it contains organic material at 1,200–1,400 μg of C per gram of soil (Table 1) and microorganisms.^{††} Like the jarosite-containing soils, no organics are detected with the Viking TV-GC-MS protocol. If the endogenous nonvolatile organics present in the Mars-1 soil simulant are thoroughly removed by organic solvent extraction, and then the dried soil is doped with stearic acid in different concentrations, the detectability of this organic material is greatly reduced when processed by TV due to the catalytic oxidation of the organics by the iron oxides present in the soil (see Fig. 4).

The results in Table 1 show two limitations of the Viking TV-GC-MS for the detection of organic material. First, when organics are present as low-level refractory substances, the temperatures reached by Viking (up to 500°C) may be inadequate to release the organics. This limitation of the Viking instrumentation was recognized but unavoidable (2), and its implications for detection of organics have been explored (10, 14). There is a second effect seen in the data in Table 1 that appears to be due to an interaction of iron in the soil with the organics during TV. The results of the jarosite and palagonite soils suggest that during TV there is an oxidation reaction of the organics catalyzed by the iron in the sample. To investigate this effect we have constructed a chemical model and an associated set of experimental simulations to determine the effect of iron compounds on 1,000 μg of C per gram of soil from stearic acid on a silica matrix during thermal heating. Fig. 5 shows the results of both the theoretical model and the experimental simulations. The thermochemical model predicts that the thermally stable oxidized carbon species at 750°C are CO_2 and CO. The lower and upper dotted lines indicate the predicted conversion to CO_2 and the sum of CO_2 and CO, respectively. In the experimental simulations, CO was not detected by TV-GC-MS possibly because it was readily oxidized to CO_2 by the water molecules absorbed in the mineral matrix from the ambient humidity. However, the oxidation of stearic acid to CO_2 falls within the predicted range, indicating that the organics are readily oxidized by TV-GC-MS, with samples containing >0.01% iron in the form of oxides or sulfate salts. A similar result is obtained at 500°C. If the samples contain higher levels of stearic acid ($\geq 1,000$ μg of C per gram of soil), then the oxidation of the organics does not go to completion in the TV step, and several

organic fragments are detected by TV-GC-MS. Therefore, the degree of attenuation of organic detection by iron compounds in the soil is not linearly dependent. Consequently TV-GC-MS *per se* is not an adequate tool for the study of organics in soils with low levels of organics and high iron content, as is expected on Mars. If the organic material is separated from the inorganic matrix by water or organic solvent extraction and then the dried residue is subjected to TV-GC-MS, a variety of organic compounds are detected (see Fig. 3).

Because carbon dioxide was replaced by hydrogen in some Viking TV-GC-MS experiments, we have investigated whether hydrogen would have counterbalanced the oxidizing power of the iron species present in the martian soil. The iron content in the soil of Mars was determined by x-ray fluorescence spectroscopy, and based on this it was inferred that Fe_2O_3 composes $\approx 19\%$ of the soil at both Viking landing sites (25). Our thermodynamic analysis shows that at the Viking temperatures (200–500°C), the reduction of hematite (Fe_2O_3) by hydrogen is thermodynamically favored; however, in the gas phase the dissociation of molecular hydrogen to atomic hydrogen (a necessary step to cause the reaction) is extremely slow at temperatures of <1,500°C (26). Hematite is known to catalyze its own reduction to wüstite (FeO) via magnetite (Fe_3O_4) in the presence of hydrogen according to the following reactions:



and

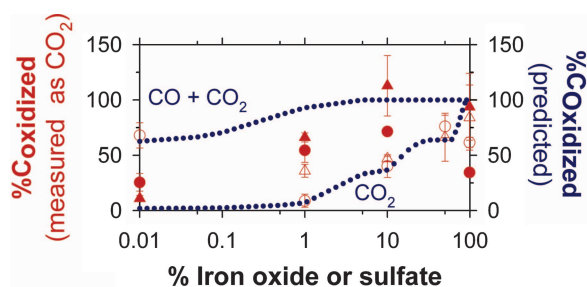
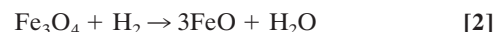


Fig. 5. Oxidation of a 1,000 μg of C from stearic acid with iron species present in silica by flash TV at 750°C in an inert atmosphere composed of helium. Symbols correspond to experimental data, and dotted lines are predicted. Open circles and triangles are Fe_2O_3 and $\text{Fe}_2(\text{SO}_4)_3$, respectively. Solid symbols indicate values of oxidation with sulfuric acid.

^{††}Mendez, C., Garza, E., Gulati, P., Morris, P. A., Allen, C. C., 36th Lunar and Planetary Science Conference, March 14–18, 2005, Houston, TX, abstr. 2360.

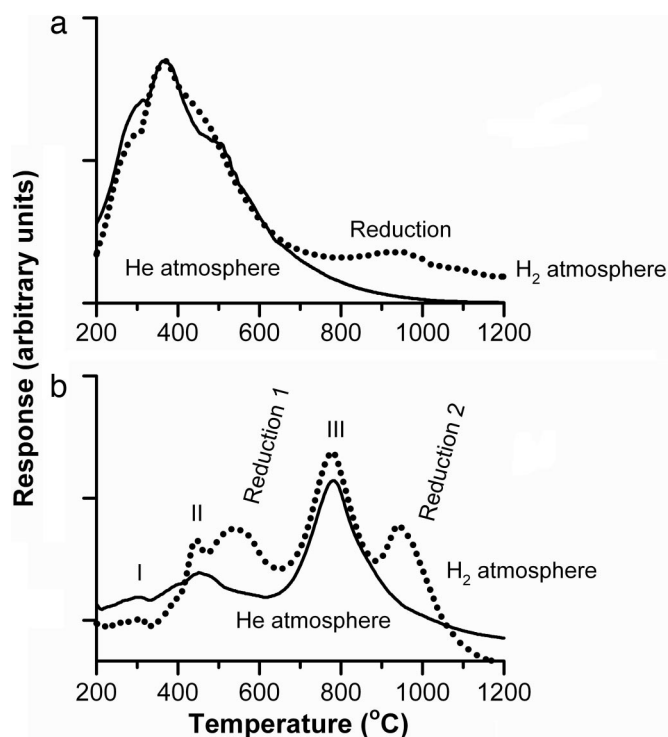
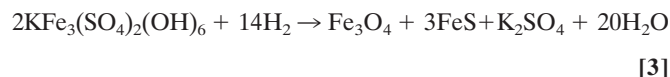


Fig. 6. MS ion current curves for water vapor as a function of temperature for the NASA Mars-1 martian soil simulant (a) and jarosite from the Panoche Valley (b). Solid lines show values for experiments run in a helium atmosphere, and dotted lines show values for experiments run in a hydrogen atmosphere.

This process takes place at temperatures of $<1,000^{\circ}\text{C}$ (27–29), but the reduction is kinetically controlled by hydrogen pressure (29) and temperature (27, 28, 30). We have experimentally studied the oxidation of hydrogen to water by the hematite present in the NASA Mars-1 martian soil simulant in the temperature range from 200°C to $1,200^{\circ}\text{C}$. The hydrogen pressure in the TV chamber was 6.4 atm (1 atm = 101.3 kPa), ≈ 13 times higher than that used in the Viking experiments (0.5 atm) (2). Fig. 6a shows the evolution of water vapor from heating the NASA Mars-1 martian soil simulant in helium and hydrogen atmospheres by TV-MS. At temperatures between 200°C and 650°C , there is a broad peak in both experiments that originates from the dehydration of the mineral phases of the soil simulant. However, at temperatures of $>650^{\circ}\text{C}$ there is a significant enhancement in the production of water in the presence of hydrogen, reaching a maximum at 930°C . This water originates from the oxidation of hydrogen catalyzed by hematite. This result is consistent with previous studies on the reduction of pure hematite, where the highest reduction rates occur at temperatures of $\geq 910^{\circ}\text{C}$ (28).

We also studied the oxidation of hydrogen to water by jarosite. Our thermodynamic analysis shows that, at the Viking temperatures (200 – 500°C), the oxidation of hydrogen to water by jarosite is thermodynamically favored. Fig. 6b shows the evolution of water vapor from heating jarosite from the Panoche Valley in helium and hydrogen atmospheres by TV-MS. In both experiments, there are three peaks at 305°C , 405°C , and 790°C that originate by the stepwise dehydration of jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. Each step involves the loss of two hydroxyl units, resulting in the formation of an oxide and the evolution of a water molecule (31). In the presence of hydrogen, there are two additional water peaks caused by the reduction of jarosite centered at 540°C and 940°C , respectively. The first reduction corresponds to the decomposition of jarosite into magnetite,

iron(II) sulfide, potassium sulfate, and water vapor, according to the following reaction:



The second reduction is due to reaction of magnetite with hydrogen according to Eq. 2.

The above experiments clearly demonstrate that shifting from carbon dioxide to hydrogen atmospheres in the Viking TV-GC-MS did not overcome the oxidizing power of the Fe_2O_3 present in the martian soil at both Viking landing sites. For jarosite-rich soils, such as those found in the Meridiani Planum site, only a slight neutralization effect occurs as a result of heating to 500°C in the presence of hydrogen.

Conclusions

Our results influence the interpretation of the Viking TV-GC-MS data. The fact that no organic molecules were released by this analytical treatment during the analysis of the Mars soils does not demonstrate that there were no organic materials on the surface of Mars because it is feasible that they were too refractory to be released at the temperatures achieved or were oxidized during the TV step by the iron present in the soil. The release of 50–700 ppm of CO_2 by TV from 200°C to 500°C in the Viking analysis (2) may indicate that an oxidation of organic material took place. The water that evolved in the volatilization experiments (0.01–1.0%) could be associated with the oxidation of hydrogen present in the organic matter by the iron oxides as well as water present in the soil. The detection of CO_2 evolving from the heating of martian samples in the TV-GC-MS experiments required a major change in the experimental procedure of the instrument. In all samples analyzed by TV-GC-MS experiments on the Viking 1 Lander and in two of nine experiments with two samples of the Viking 2 Lander, the martian soil was heated in a $^{13}\text{CO}_2$ atmosphere. H_2 , which was the carrier gas for the gas chromatograph, was not used to avoid the possible catalytic or thermally induced reduction of organic material possibly present in the sample (2). However, in an effort to lower the detection limit for the most volatile components, H_2 was used in two sample experiments (2). The source of the H_2 was the gas chromatograph carrier gas, and the net hydrogen pressure in the sample oven was ≈ 0.5 atm. Our thermodynamic analysis shows that, at the Viking temperatures (200 – 500°C), the reduction of iron oxides by hydrogen is thermodynamically favored; however, our experimental data indicate that the reaction is kinetically controlled and does not occur at temperatures of $<650^{\circ}\text{C}$. Therefore, it seems unlikely that hydrogen could have neutralized the oxidizing power of the Fe_2O_3 present in the martian soil. The CO_2 released from the thermal treatment of the martian soil could have also originated from an inorganic source, such as carbonates (2); however, carbonate minerals do not seem to be important in the martian environment (32). Thermal IR spectra of the martian surface indicate the presence of small concentrations (≈ 2 –5 wt %) of carbonates, specially dominated by magnesite, MgCO_3 (33). Because magnesite starts to decompose into magnesium oxide (MgO) and CO_2 at $\geq 490^{\circ}\text{C}$ (34) and considering that the amount of CO_2 released in the martian soil did not change from 350°C to 500°C (2), we can conclude that the effect of magnesite in the martian soil at Viking Landing Site 2 was negligible. Certainly most of the CO_2 and H_2O detected by the Viking TV-GC-MS was derived from desorption from the soil as suggested (2). We are demonstrating that some fraction could have been derived from oxidation of organics. Therefore, the question of whether organic compounds exist on the surface of the planet Mars was not conclusively answered by the organic analysis experiment carried out by the Viking Landers. Further-

more, it is important that future missions to Mars include other analytical methods to search for extinct and/or extant life in the martian soil. The Thermal Evolved Gas Analyzer instrument on NASA's 2007 Mars Scott Phoenix mission is a TV-MS for the analysis of water, carbon dioxide, and volatile organics (35). The Sample Analysis at Mars Instrument Suite for the upcoming NASA 2009 Mars Science Laboratory mission will include laser desorption MS for analysis of insoluble refractory organics, solvent extraction followed by chemical derivatization coupled to GC-MS, and TV-GC-MS for the analysis of soluble and insoluble organics, respectively.^{††} The Mars Organic Detector for the European Space Agency ExoMars mission scheduled for launch in 2011 or 2013 will include a TV chamber connected to a cold finger for the sublimation of amino acids and polycyclic aromatic hydrocarbons, which will then be analyzed by capillary electrophoresis using a fluorescence detector (36).

Materials and Methods

For further detail, see *Supporting Materials and Methods*, which is published as supporting information on the PNAS web site. Total organic matter was determined by titration with the oxidation of permanganate and by its oxidation to carbon dioxide followed by GC (model no. HP-5890; Hewlett-Packard, Palo Alto, CA) MS (model no. HP-5989B; Hewlett-Packard)

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analysis. Elemental analysis was done with a model EA1108 analyzer (Fisons, Loughborough, U.K.) at 1,200°C. TV-GC-MS was performed with a coil filament-type pyrolyzer (Pyroprobe 2000; CDS Analytical, Inc., Oxford, PA) coupled to GC-MS (model nos. HP-5890 and HP-5989B). Organics from the soil were extracted by a Soxhlet system with methylene chloride/methanol (2:1) over 8 h, and the dried residue was analyzed by ¹H NMR (Eclipse 300-MHz spectrometer; JEOL, Ltd., Tokyo, Japan), Fourier transform IR spectroscopy (Tensor 27 spectrometer; Bruker, Billerica, MA), and by TV-GC-MS with a ribbon element probe for direct deposition. The carbon isotope analysis was performed with MS (Delta Plus XL analyzer; Finnigan, Bremen, Germany) equipped with a Flash 1112EA elemental analyzer. Hydrogen oxidation of soil analogs was carried out by replacing helium with hydrogen in the oven of the TV-MS analysis. Thermochemical modeling was carried out with the FactSage software package.

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